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(71) Applicant : **The Lubrizol Corporation**  
**29400 Lakeland Boulevard**  
**Wickliffe, Ohio 44092 (US)**

(72) Inventor : **Konzman, Edward Joseph**  
**1061 East 346 Street**  
**Eastlake, Ohio 44095 (US)**

(74) Representative : **Mallalieu, Catherine Louise et al**  
**D. Young & Co.,**  
**21 New Fetter Lane**  
**London EC4A 1DA (GB)**

(54) **Functional fluids with improved thermal stability and hydrolytic stability.**

(57) A functional fluid which includes an oil and an additive composition of a metal salt of a thiophosphorus acid and a salt of a salicylic acid exhibits improved thermal and hydrolytic stability, even in the presence of acid rust inhibitors.

The present invention relates to a functional fluid which includes an additive composition of a metal salt of a thiophosphorus acid and a salt of a salicylic acid.

The use of metal salts, especially zinc salts, of sulfur and phosphorus containing acids as antioxidants and extreme pressure agents in lubricants and functional fluids has been known for some time. However, the environment in which such fluids are used has become increasingly severe over recent years with further development of machinery employing such fluids. It is increasingly important that materials of this type have high thermal and hydrolytic stability. There have been several attempts to provide improved stability to such materials.

PCT application WO 89/04358, published May 18, 1989, discloses a functional fluid which includes a composition of (A) at least one neutral or basic metal salt or boron-containing neutral or basic metal salt of at least one organic compound; (B) at least one metal deactivator; and (C) at least one compound selected from phosphorus-containing amide, phosphorus-containing ester, sulfur coupled dithiocarbamate, and sulfur containing compound of formula (I). The neutral or basic metal salt of (A) can be an alkali metal, alkaline earth metal, zinc, copper, aluminum (or mixture) salt of e.g. a carboxylic acid. The carboxylic acid can be a salicylic acid. Compositions including magnesium salicylate (detergent) and a rust inhibitor are disclosed. The material of (A) can likewise be based on an O,O-dihydrocarbyl phosphorodithioic acid. Extreme pressure agents, corrosion-inhibiting agents, and antioxidants may be included, for example zinc dialkylphosphorodithioates.

U.S. Patent 4,282,106, Schaap et al., August 4, 1981, discloses an engine oil resistant to oxidation, including a lubricating oil stock, a sulfurized oil, a dispersant, an anti-corrosion agent such as metal dithiophosphates, an anti-rust agent, a detergent such as neutral or overbased sulfonates, phosphonates, thiosphosphonates, sulfurized phenates, or salicylates, an anti-oxidant, and a viscosity index improver.

U.S. Patent 3,410,798, Cohen, November 12, 1968, discloses basic metal salts of phenol or salicylic acid sulfides which are useful as detergent additives for lubricants. Other additives include zinc di-(isooctyl)phosphorodithioate.

U.S. Patent 2,261,047, Asseff, October 28, 1941, discloses lubricants which contain a zinc salt of an acidic reaction product obtained by reacting phosphorus pentasulfide with a cyclo-aliphatic alcohol. The lubricant can also contain oil-soluble metallic phenates such as those derived from such phenolic compounds as esters of salicylic acid.

U.S. Patent 3,761,404, Calow et al., September 25, 1973, discloses a lubricant composition including a salt of a divalent metal and an alkylsalicylic acid. Other additives such as zinc dialkyl dithiophosphates may be present.

U.S. Patent 4,627,928, Karn, December 9, 1986, discloses basic magnesium salts of substituted aromatic hydroxy carboxylic acids (e.g. salicylic acids) which can be used in lubricating oils. A zinc dialkylphosphorodithioate can also be present.

U.S. Patent 4,466,894, Grover, August 21, 1984, discloses functional fluids containing (A) at least one metal (preferably zinc) salt of a mixture of acids comprising a phosphorodithioic acid and an aliphatic or alicyclic carboxylic acid, (B) a sulfurized Group II metal phenate, and (C) a triazole.

U.S. Patent 4,417,990, Clason et al., November 29, 1983, discloses functional fluids containing (A) a mixed metal (preferably zinc) salt of a phosphorodithioic acid and an aliphatic or alicyclic carboxylic acid containing 2-40 carbon atoms, and (B) a sulfurized Group II metal phenate.

U.S. Patent 4,308,154, Clason et al., December 29, 1981, discloses mixed metal salts (especially zinc salts) of dialkylphosphorodithioic acids and carboxylic acids in a ratio of about 0.5:1 to about 4.5:1, useful in functional fluids such as hydraulic fluids as antioxidants and extreme pressure agents having improved thermal stability.

The term "functional fluid" includes hydraulic fluids and refers generally to fluids which serve to function by virtue of their bulk or fluid properties. This is in contrast to other materials, such as lubricants for e.g. internal combustion engines, which are used primarily to impart lubricity to moving surfaces without much regard for the properties of the composition as a fluid. Of course, functional fluids often must serve a secondary purpose of providing lubrication to parts in which they come in contact.

Functional fluids have been found to suffer from lack of thermal and hydrolytic stability in particular when certain rust inhibitors are present, especially acidic rust inhibitors. Such instability is also often observed when certain antiwear additives are present, particularly metal salts or esters of thiophosphorus acids; the instabilities are often worse when both classes of materials are present in the same fluid. The present invention now provides a functional fluid composition which exhibits improved thermal and hydrolytic stability, by incorporating into the functional fluid a small amount of a salt of a salicylic acid.

According to one aspect the present invention provides a functional fluid comprising a major amount of an oil of lubricating viscosity, at least one metal salt of a thiophosphoric acid or a mixture of a thiophosphorus acid and a carboxylic acid, an alkali, alkaline earth, or transition metal salt of a salicylic acid, and a rust inhibitor,

provided that the functional fluid contains less than about 1% by weight of a dispersant and less than about 1% by weight of a basic sulfonate salt.

In another embodiment the invention provides a functional fluid comprising a major amount of an oil of lubricating viscosity, from about 0.1% to about 2% by weight of a basic metal salt of a thiophosphoric acid or a combination of a thiophosphoric acid and a carboxylic acid, from about 0.001% to about 1% by weight of an alkali, alkaline earth, or transition metal salt of a salicylic acid, and at least one acidic rust inhibitor.

The invention further provides a method of improving thermal stability of a functional fluid, comprising the steps of preparing a mixture of a major amount of an oil of lubricating viscosity and a minor proportion of the above composition.

Another embodiment of the invention provides a concentrate comprising about 3 to about 50 percent by weight of a carrier and about 50 to about 97 percent by weight of a mixture of at least one metal salt of a thiophosphoric acid or a mixture of a thiophosphorus acid and a carboxylic acid; and an alkali, alkaline earth, or transition metal salt of a salicylic acid, provided that the concentrate contains less than about 5% by weight of a dispersant and less than about 5% by weight of a basic sulfonate salt.

Yet another embodiment of the present invention is an aqueous based functional fluid comprising water, about 2 to about 10 weight percent of the composition of the aforementioned concentrate, and about 1 to about 5 weight percent of an emulsifier.

Various preferred features and embodiments of the present invention will now be described by way of non-limiting example.

The oil of lubricating viscosity. The first and major component of this invention is an oil of lubricating viscosity, including natural or synthetic lubricating oils and mixtures thereof. Natural oils include animal oils, vegetable oils, mineral lubricating oils of paraffinic, naphthenic, or mixed types, solvent or acid treated mineral oils, and oils derived from coal or shale. Synthetic lubricating oils include hydrocarbon oils, halo-substituted hydrocarbon oils, alkylene oxide polymers (including those made by polymerization of ethylene oxide or propylene oxide), esters of dicarboxylic acids and a variety of alcohols including polyols, esters of monocarboxylic acids and polyols, esters of phosphorus-containing acids, polymeric tetrahydrofurans, and silicon-based oils (including siloxane oils and silicate oils). Included are unrefined, refined, and rerefined oils. Specific examples of the oils of lubricating viscosity are described in U.S. Patent 4,326,972.

The oil comprises a major amount of the composition. This means that normally the amount of oil is at least 50% of the composition. Depending on the particular application, the amount of oil in the composition may be much greater than this amount. Commonly the amount of oil is 90-99.8%, preferably 96-99.5%. In practice the amount of oil will normally be the amount required to complete formulation to 100% after the active components, discussed below, are supplied. It is noted that many of the additive components described below are available commercially in a form which may contain up to 60 percent by weight or more of so-called diluent oil. The diluent oil is normally an ordinary mineral oil which is present for ease of formulation and handling. Unless otherwise indicated, in this specification the amount of each active component is described on an oil-free basis; any diluent oil present in the commercial material is considered to contribute to the total amount of oil of lubricating viscosity.

Alternatively, the composition of the present invention can be prepared as a concentrate, using only a relatively small amount of oil (or other solvent or carrier), i.e., an amount sufficient to assure ease of handling and mixing of the remaining components. When such a concentrate is prepared the relative amounts of the other components will remain about the same as is described hereinbelow, but their absolute amounts will become proportionately greater as the amount of carrier is reduced. Typically in such a concentrate the amount of carrier is 3 to 50 percent by weight of the total concentrate composition, and preferably 10 to 20 percent by weight; the active ingredients comprise the complementary amount.

If a concentrate is prepared, the carrier is most conveniently an oil, as described above, although other materials can be used. If a material other than an oil is used, it should be a substance in which the additive components are soluble or readily dispersable, and it should likewise be soluble or readily dispersable in the oil of the final composition and not harmful to the final composition. Suitable non-oil carriers include organic materials which are generally substantially non-polar or non-protic materials, preferably those which are liquids at room temperature. Such materials can include alkanes and halo alkanes of 5 to 18 carbon atoms, polyhaloalkanes, cycloalkanes of 5 or more carbon atoms, alkyl or halo substituted alkanes, aryl hydrocarbons, alkylaryl hydrocarbons, haloaryl hydrocarbons, ethers such as dialkyl ethers, alkyl aryl ethers, cycloalkyl ethers, alkanolic acid esters, silicate esters, and mixtures of these. Also useful can be low molecular weight liquid polymers, generally classified as oligomers, including dimers, tetramers, pentamers, etc., including such materials as propylene tetramers and isobutylene dimers. Also useful are liquid petroleum fractions such as naphthene-based or paraffin-based petroleum fractions.

If a concentrate is used, the final functional fluid composition will normally be prepared by adding an ap-

appropriate amount of the concentrate to the oil of lubricating viscosity and mixing, so that the appropriate amount of additives are imparted to the oil.

#### The thiophosphorus salt.

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The composition of the present invention also includes at least one metal salt of a thiophosphoric acid or a mixture of a thiophosphorus acid and a carboxylic acid. As used herein, the term "thiophosphorus" means that the compound contains phosphorus and sulfur, without specifying the oxidation state of the phosphorus.

The thiophosphorus acid can be a monothiophosphoric acid or a dithiophosphoric acid (also referred to as a phosphorodithioic acid). Most commonly the thiophosphorus acid component will be at least one metal salt of a dihydrocarbyl dithiophosphoric acid. The phosphorodithioic acids from which the metal salts useful in this invention are prepared can be obtained by the reaction of about 4 moles of an alcohol mixture per mole of phosphorus pentasulfide, and the reaction may be carried out within a temperature range of from about 50° to about 200°C. The reaction generally is completed in about 1 to 10 hours, and hydrogen sulfide is liberated during the reaction.

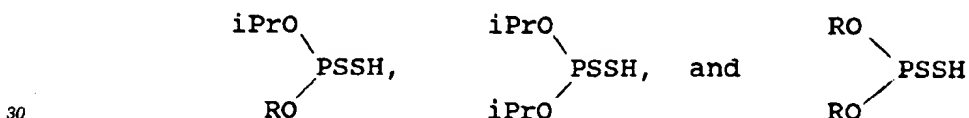
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The alcohols which may be included in the alcohol mixture include primary alcohols such as n-butyl alcohol, isobutyl alcohol, n-amyl alcohol, isoamyl alcohol, n-hexyl alcohol, 2-ethyl-1-hexyl alcohol, isooctyl alcohol, nonyl alcohol, decyl alcohol, dodecyl alcohol, tridecyl alcohol, etc. The alcohols also may contain various substituent groups such as halogens. Particular examples of useful mixtures include isopropyl/n-butyl; isopropyl/secondary butyl; isopropyl/2-ethyl-1-hexyl; isopropyl/isooctyl; isopropyl/decyl; isopropyl/dodecyl, and isopropyl/tridecyl alcohols.

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The composition of the phosphorodithioic acid obtained by the reaction of a mixture of alcohols (e.g. iPrOH and ROH) with phosphorus pentasulfide is actually a statistical mixture of three or more phosphorodithioic acids as illustrated by the following formulae:

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In the present invention it is preferred to select two or more alcohols reacted with the  $\text{P}_2\text{S}_5$  to result in a mixture in which the predominating dithiophosphoric acid is the acid (or acids) containing one isopropyl group and one primary alkyl group. Relative amounts of the three phosphorodithioic acids in the statistical mixture is dependent, in part, on the relative amounts of the alcohols in the mixture, steric effects, etc. The alcohol mixture can also contain a mixture of aliphatic alcohols and aromatic alcohols (phenols). Thus the phosphorus containing acid, in a preferred embodiment, will contain an aliphatic group and an aromatic group or at least two aliphatic groups, which can be derived from the alcohols described above. In one embodiment the alcohols used comprise at least 10 mole percent of isopropyl alcohol and at least one primary alcohol containing from about 3 to about 13 carbon atoms.

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If the acid used is not specifically a thiophosphoric acid but is more generally a thiophosphorus acid, then the acid will be a mixture of the thiophosphorus acid and a carboxylic acid. Carboxylic acids may also be present, however, if a thiophosphoric acid is used. Suitable carboxylic acids include aromatic, aliphatic, heterocyclic, and alicyclic carboxylic acids, both mono acids and polyacids (containing more than one carboxylic acid group per molecule) and both saturated and unsaturated acids. These carboxylic acids include lower molecular weight carboxylic acids (e.g., carboxylic acids having up to about 22 carbon atoms such as acids having about 4 to about 22 carbon atoms or tetrapropenyl-substituted succinic anhydride) as well as higher molecular weight carboxylic acids.

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Examples of useful acids include dodecanoic acid, decanoic acid, oleic acid, stearic acid, linoleic acid, tall oil acid, 10-methyl-tetradecanoic acid, 3-ethyl-hexadecanoic acid, 8-methyl-octadecanoic acid, isoaliphatic acids including mixtures of branch-chain acids prepared by the isomerization of commercial fatty acids (oleic, linoleic or tall oil acids) of, for example, about 16 to about 20 carbon atoms, palmitic acid, stearic acid, myristic acid, oleic acid, linoleic acid, behenic acid, hexatriacontanoic acid, tetrapropenyl-substituted glutaric acid, polybutenyl-substituted succinic acid derived from a polybutene ( $M_n = 200-1500$ , preferably 300-1000), polypropenyl-substituted succinic acid derived from a polypropene, ( $M_n = 200-1000$ , preferably 300-900), octadecyl-substituted adipic acid, chlorostearic acid, 9-methylstearic acid, dichlorostearic acid, stearyl-benzoic acid, eicosanyl-substituted naphthoic acid, dilauryl-decahydronaphthalene carboxylic acid, mixtures of any of these acids, their alkali and alkaline earth metal salts, and/or their anhydrides. A preferred group of aliphatic car-

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boxylic acids includes the saturated and unsaturated higher fatty acids containing from about 12 to about 30 carbon atoms. Illustrative of these acids are lauric acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, oleostearic acid, stearic acid, myristic acid, and undecalnic acid, alpha-chlorostearic acid, and alphanitrolauric acid. Examples of aromatic acids include substituted and non-substituted benzoic, phthalic and salicylic acids or anhydrides, where the substituents can be, for example, butyl, isobutyl, pentyl, octyl, nonyl, dodecyl, 5-chlorohexyl, 4-ethoxypentyl, 3-cyclohexyloctyl, 2,3,5-trimethylheptyl, and substituents derived from polymerized olefins. Salicylic acid and substituted salicylic acids may also be employed.

Highly preferred carboxylic acids are those containing 2 to 40 carbon atoms, and especially 5 to 12 carbon atoms. All the above-described acids are well known in the art.

The metal used to make the salt of the above acids is preferably a Group II metal, aluminum, tin, iron, cobalt, lead, molybdenum, manganese, nickel, zinc, or copper. Most preferably the metal is zinc. Examples of metal compounds which may be reacted with the acid include silver oxide, silver carbonate, magnesium oxide, magnesium hydroxide, magnesium carbonate, magnesium ethylate, calcium oxide, calcium hydroxide, zinc oxide, zinc hydroxide, strontium oxide, strontium hydroxide, cadmium oxide, cadmium carbonate, barium oxide, barium hydrate, aluminum oxide, aluminum propylate, iron carbonate, copper hydroxide, lead oxide, tin butylate, cobalt oxide, nickel hydroxide, etc.

The preparation of the metal salt of the dithiophosphoric acids may be effected by reaction with the metal or metal oxide. Simply mixing and heating these two reactants is sufficient to cause the reaction to take place and the resulting product is sufficiently pure for the purposes of this invention. Typically the formation of the salt is carried out in the presence of a diluent such as an alcohol, water, or diluent oil. Neutral salts are prepared by reacting one equivalent of metal oxide or hydroxide with one equivalent of the acid. Basic metal salts are prepared by adding an excess of (more than one equivalent of) the metal oxide or hydroxide with one equivalent of phosphorodithioic acid. Detailed examples of the preparation of such salts are presented in U.S. Patent 4,981,602.

Generally, the compositions of the present invention will contain varying amounts of one or more of the above-identified metal dithiophosphates or mixtures thiophosphorus and carboxylic salts, the total of such salts being normally in the range of 0.05 to 2% by weight of the total composition, and preferably 0.1 to 1% by weight.

#### The salt of a salicylic acid

The composition of the present invention further comprises a zinc salt of a salicylic acid. The salicylic acids preferably are hydrocarbyl-substituted salicylic acids, preferably aliphatic hydrocarbon-substituted salicylic acids wherein each substituent contains an average of at least 8 carbon atoms per substituent and 1 to 3 substituents per molecule. The substituents can likewise be polyalkene substituents, where polyalkenes include homopolymers and interpolymers of polymerizable olefin monomers of 2 to about 16, preferably 2 to 6, or 2 to 4 carbon atoms. The olefins may be monoolefins such as ethylene, propylene, 1-butene, isobutene, and 1-octene; or a polyolefinic monomer, such as diolefinic monomer, such 1,3-butadiene and isoprene. In one embodiment, the interpolmer is a homopolymer. An example of a homopolymer is a polybutene. In one instance about 50% of the polybutene is derived from isobutylene.

It is preferred that the hydrocarbyl substituent group or groups on the salicylic acid contains 7 to 300 carbon atoms. It is more preferred that the hydrocarbyl group is an alkyl group having a molecular weight of 150 to 2000. The polyalkenes and polyalkyl groups are prepared by conventional procedures, and substitution of such groups onto salicylic acid can be effected by known methods.

The salicylic acid is in the form of a zinc salt, which is formed by known neutralization techniques from a basic zinc compound.

It is also permissible that the salt of the salicylic acid be a basic metal salt, also known as an overbased salt. Overbased salts are known in the art, having been described in 1954 in U.S. patent 2,695,910. They are essentially complexes of certain organic acids having metal contents which are greater than the stoichiometric amount required to neutralize the acid. Such materials are referred to in the art as overbased, superbased, hyperbased, and so on.

The terminology "metal ratio" is used in the prior art and herein to designate the ratio of the total chemical equivalents of the metal in the overbased material (e.g. a metal sulfonate, carboxylate, phosphate, or phenate) to the chemical equivalents of the metal in the product which would be expected to result from the reaction between the organic material to be overbased (i.e. the salicylic acid) and the metal containing reactant (a hydroxide, oxide, etc.) according to known chemical reactivity and stoichiometry of the two reactants. Thus in normal or neutral calcium sulfonate the metal ratio is one and in an overbased calcium sulfonate the metal ratio is greater than one, e.g. 4.5. Obviously, if there is present in the material to be overbased more than one

compound capable of reacting with the metal, the metal ratio of the product will depend on whether the number of equivalents of metal in the overbased product is compared to the number of equivalents expected to be present for a given single component or a combination of all such components.

The overbased materials generally are prepared by treating a reaction mixture comprising the salicylic acid to be overbased, a reaction medium consisting essentially of at least one inert organic solvent for the organic material, a stoichiometric excess of a metal base, a promoter, and an acid material. The methods for preparing the overbased materials as well as a diverse group of overbased materials are well known in the art and are disclosed for example in U.S. patent 4,728,578. Briefly, a salicylic acid is selected which is generally soluble in the reaction medium to be employed, normally a mineral oil.

Promoters which permit the incorporation of the excess metal into the overbased material are also well known. They include alcoholic and phenolic promoters such as methanol, ethanol, amyl alcohol, octanol, isopropanol, hydroxy substituted benzenes or naphthalenes, heptylphenols, octylphenols, nonylphenols, and mixtures of the above.

Another component of the overbased material is an acidic material (distinct from the organic acid which is referred to as the overbased acid). Included within the known group of useful acidic materials are liquid acids such as formic acid, acetic acid, nitric acid, sulfuric acid, sulfurous acid, boric acid, phosphoric acid, phosphorous acid, hydrochloric acid, hydrobromic acid, carbamic acid, substituted carbamic acids, etc. The preferred acidic material is carbon dioxide.

In preparing overbased materials, the organic acid to be overbased is brought together in an inert non-polar organic liquid carrier or solvent, with the metal base, the promoter, and the acidic material (CO<sub>2</sub>), and a chemical reaction ensues. The reaction temperature is usually about 27 - 159°C (80° - 300°F), more often about 38 - 93°C (100° - 200°F). The exact nature of the resulting overbased product is not known, but it can be described as a single phase homogeneous mixture of the solvent and either (1) a metal complex formed from the metal base, the acidic material, and the organic acid and/or (2) an amorphous metal salt formed from the reaction of the acid material with the metal base and the organic acid.

The salt of the salicylic acid is present in the composition of the present invention in an amount of 0.001% to 1% based on the weight of the composition, and preferably 0.01 to 0.5% by weight.

The presence of the salt of the salicylic acid in the functional fluid leads to improved thermal stability (as measured by e.g. sludge formation) and hydrolytic stability in the functional fluids.

#### Rust inhibitors.

In a preferred embodiment of the invention, the composition also contains a rust inhibitor other than the components set forth above. Rust inhibitors, and in particular acidic rust inhibitors, are important in many functional fluid applications, yet when they are present they may adversely affect the thermal stability of the composition. It is in these instances where the present invention is most clearly useful for providing improved thermal stability.

Rust inhibitors include hydrocarbyl sulfonate salts, esters of amino acids, esters of fatty acids, particularly esters of C<sub>12</sub>-C<sub>24</sub> fatty acids, hydrocarbyl substituted carboxylic acids, hydrocarbyl substituted amides, hydrocarbyl substituted imidazolines, hydrocarbyl substituted oxazolines, and hydrocarbyl esters of phosphoric acid. A preferred class of acid rust inhibitors includes half esters of hydrocarbyl-substituted succinic acids. Specific examples include alkyl esters (particularly the propyl ester) of C<sub>12</sub> alkyl substituted succinic acid and esters prepared by reacting alkylene oxides with alkyl substituted succinic acid. These and related rust inhibitors are described in more detail in U.S. Patent 3,062,443.

The preferred amount of rust inhibitor, if present, is an amount which reveals the need for and the beneficial effect of the composition of the present invention. Preferably the amount of rust inhibitor is 0.01 to 1% by weight of the fully formulated composition, more preferably 0.03 to 0.2% by weight.

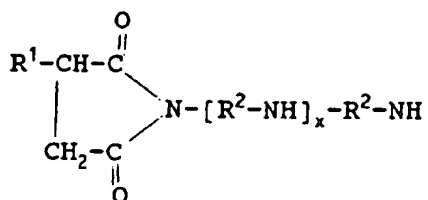
#### Miscellaneous additives.

The composition of the present invention also may contain other customary additives in customary amounts, including antioxidants, corrosion inhibitors, extreme pressure agents, and anti-wear agents, pour point depressants, and anti-foam agents.

The composition of the present invention, however, normally contains less than 1% by weight of a dispersant and less than 1% by weight of a basic sulfonate salt, and is preferably substantially free from such materials. Such materials are often present in lubricants for internal combustion engines, but their presence is unnecessary and may even be detrimental for other applications such as the functional fluids of the present invention.

Dispersants are well known in the field of lubricants and include primarily what is known as ashless-type dispersants and polymeric dispersants. Sometimes metal salts in general, and overbased metal salts in particular, have been referred to in the literature as "dispersants," but they are more properly and commonly referred to as "detergents," and such materials are not intended to be encompassed by the term "dispersants."

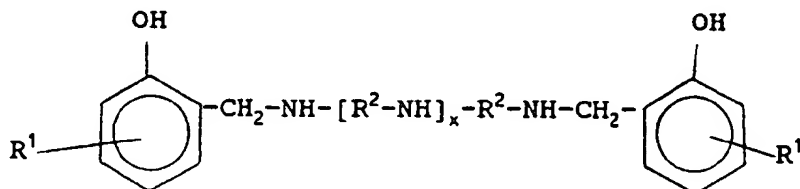
Ashless type dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include N-substituted long chain alkenyl succinimides, having a general formula



where R<sup>1</sup> is an alkyl group, frequently a polyisobutyl group with a molecular weight of 800-1200, and R<sup>2</sup> are alkenyl groups, commonly ethylenyl (C<sub>2</sub>H<sub>4</sub>) groups. Such molecules are commonly derived from reaction of an alkenyl acylating agent with a polyamine, and a wide variety of linkages between the two moieties is possible beside the simple imide structure shown above, including a variety of amides and quaternary ammonium salts. Succinimide dispersants are more fully described in U.S. Patent 4,234,435.

Another class of ashless dispersant is high molecular weight esters. These materials are similar to the above-described succinimides except that they may be seen as having been prepared by reaction of a hydrocarbyl acylating agent and a polyhydric aliphatic alcohol such as glycerol, pentaerythritol, or sorbitol. Such materials are described in more detail in U.S. Patent 3,381,022.

Another class of ashless dispersant is Mannich bases. These are materials which are formed by the condensation of a higher molecular weight, alkyl substituted phenol, an alkylene polyamine, and an aldehyde such as formaldehyde. Such materials may have the general structure



(including a variety of isomers and the like) and are described in more detail in U.S. Patent 3,634,515.

Other dispersants include polymeric dispersant additives, which are generally hydrocarbon-based polymers which contain polar functionality to impart dispersancy characteristics to the polymer.

Basic sulfonate salts, which are also to be avoided for purposes of the present invention, are overbased materials (described generally above in the context of salicylates) which result from the reaction of a sulfonic acid with excess basic material. Sulfonic acids include the mono- or polynuclear aromatic or cycloaliphatic compounds. The sulfonates are normally oil-soluble materials which can be represented for the most part by one of the following formulae: R<sub>2</sub>-T-(SO<sub>3</sub>)<sub>a</sub> and R<sub>3</sub>-(SO<sub>3</sub>)<sub>b</sub>, wherein T is a cyclic nucleus such as, for example, benzene, naphthalene, anthracene, diphenylene oxide, diphenylene sulfide, petroleum naphthenes, etc.; R<sub>2</sub> is an aliphatic group such as alkyl, alkenyl, alkoxy, alkoxyalkyl, etc.; (R<sub>2</sub>)+T contains a total of at least about 15 carbon atoms; and R<sub>3</sub> is an aliphatic hydrocarbyl group containing at least about 15 carbon atoms. Examples of R<sub>3</sub> are alkyl, alkenyl, alkoxyalkyl, carboalkoxyalkyl, etc. Specific examples of R<sub>3</sub> are groups derived from petrolatum, saturated and unsaturated paraffin wax, and the above-described polyalkenes. The groups T, R<sub>2</sub>, and R<sub>3</sub> in the above Formulae can also contain other inorganic or organic substituents in addition to those enumerated above such as, for example, hydroxy, mercapto, halogen, nitro, amino, nitroso, sulfide, disulfide, etc. In the above Formulae, a and b are at least 1. In one embodiment, the sulfonic acids have a substituent (R<sub>2</sub> or R<sub>3</sub>) which is derived from one of the above-described polyalkenes.

#### Aqueous compositions.

In addition to the oil-based compositions which have been described in detail above, it is also possible to

prepare aqueous compositions of the present invention. These compositions are normally prepared from a concentrate of the active components in a carrier fluid, which has been described above, but they can also be prepared by mixing the active components directly in water. In either case, in order to provide for adequate mixing and dispersion of the components in the aqueous medium, an emulsifier is normally used. Suitable emulsifiers include anionic agents such as carboxylic acids, sulfuric acid esters, alkane sulfonic acids, alkyl aromatic sulfonic acids, phosphates and phosphonic acids, persulfates, thiosulfates, sulfonamides, and sulfamic acids. Cationic emulsifying agents include primary, secondary, and tertiary amine salts, quaternary ammonium compounds, other nitrogenous bases such as guanidine, and thiuronium salts, non-nitrogenous bases such as phosphonium compounds and sulfonium compounds. Nonionic emulsifying agents include compounds with ether, ester, or amide linkages. Ampholytic emulsifying agents include amino-carboxy compounds, amino-sulfuric acid ester compounds, amino-alkane sulfonic acid compounds, and amino-aromatic sulfonic acid compounds. More specifically one can mention sulfonate salts, salts of fatty acids, esters such as sorbitan monoleate, and polyalkylene glycols. Suitable concentrations of the emulsifying agent are those which are suitable to provide for dispersing the active ingredients and oil or other carrier (if any) into the water. Often the amount of emulsifying agent required will be somewhat less than the amount of the materials to be dispersed. Thus an aqueous based functional fluid comprising water and 2 to 10 weight percent of a concentrate as described above would be expected to also include 1 to 5 weight percent of an emulsifier.

The compositions of the present invention are useful as functional fluids, that is, especially as hydraulic fluids, but also as turbine oils, compressor fluids, heat transfer fluids, metalworking fluids, high-water based hydraulic fluids, bearing oils, gear oils, and rust and oxidation inhibited oils.

As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" means a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Such groups include hydrocarbon groups, substituted hydrocarbon groups, and hetero groups, that is, groups which, while primarily hydrocarbon in character, contain atoms other than carbon present in a chain or ring otherwise composed of carbon atoms.

## EXAMPLES

### Example 1.

A composition is prepared by mixing 0.42 parts by weight of zinc dialkyldithiophosphate (where the alkyl groups are mixed propyl and 2-ethylhexyl groups) with 0.05 parts of a neutral zinc salt of alkyl salicylic acid, the alkyl group having a number average molecular weight of about 900, the alkyl group having about 13 to about 18 carbon atoms.

### Example 2.

A composition is prepared by mixing a mineral oil with 0.05 weight % of the half methyl ester of mixed alkyl succinic anhydrides where the alkyl groups contain about 8-20 carbon atoms (averaging 12). To this composition is added 0.47 weight % of the product of Example 1.

### Example 3.

A concentrate is prepared by mixing 56.2 weight % of zinc O,O-di(2-ethylhexyl)dithiophosphate, 21.2 weight % 2,6-di-t-butylphenol, 0.5 weight % ethoxylated alcohol demulsifier, 3.9 weight % (on an oil-free basis) of overbased sulfurized calcium dodecylphenate (prepared by reacting dodecylphenol with a sulfur source, neutralizing the product with excess calcium oxide or hydroxide in an oil medium, and treating the basic mixture with carbon dioxide gas to yield the overbased carbonate salt having a metal ratio of about 3.2), 1.3 weight % of a neutral zinc salt of alkyl salicylic acid, the alkyl group having about 13 to about 18 carbon atoms, and about 16 weight percent diluent mineral oil.

### Example 4.

A fully compounded hydraulic fluid is prepared by admixing 0.85 weight % of the concentrate of Example 4 in a petroleum oil of lubricating viscosity.



Example 5 (comparative).

A composition is prepared from 0.11 weight percent zinc O,O-di(isopropyl)dithiophosphate, 0.31 weight percent zinc O,O-di(2-ethylhexyl)dithiophosphate, 0.32 weight percent of the reaction product of dodecyl substituted succinic anhydride, propylene oxide, and a small amount of water (to form a partial ester) and the balance mineral oil.

Example 6.

Example 5 is substantially repeated except that in addition 0.04 weight percent of a zinc salt of alkyl salicylic acid, the alkyl group having about 13 to about 18 carbon atoms, is added. The composition exhibits good hydrolytic stability.

Example 7.

Example 5 is substantially repeated except that in addition 0.125 weight % of a zinc salt of alkyl salicylic acid, the alkyl group having about 13 to about 18 carbon atoms, is added. The composition exhibits good hydrolytic and thermal stability.

Example 8. (comparative).

A composition is prepared from 0.48 weight % of a zinc salt of mixed alkyl dithiophosphate, 0.0015 weight percent tolyltriazole, 0.18 weight % di-t-butylphenol, 0.004 weight % ethoxylated alcohol demulsifier, 0.03 weight % overbased sulfurized calcium dodecylphenate as in Example 3, 0.015 weight % neutral calcium dinonyl naphthalene sulfonate rust inhibitor, and the balance mineral oil.

Example 9.

Example 8 is substantially repeated except that in addition 0.003 weight % of the zinc salt of an alkyl substituted salicylic acid, the alkyl group having 13-18 carbon atoms, is added. The composition exhibits low sludge in a thermal stability test.

Examples 10-12.

Example 9 is repeated except that the tolyltriazole is replaced by each of the triazoles from the following list, in turn:

- 10: benzotriazole
- 11: N-methylbenzotriazole
- 12: xyliltriazole.

Examples 13 - 19.

Example 2 is repeated except that the half ester of the alkyl succinic anhydride is replaced by each of the following in turn:

- 13: octadecylimidazoline;
- 14: calcium mixed hydrocarbyl sulfonates where the hydrocarbyl groups are a mixture of C-12 to C-24 alkyl and alkylaryl groups;
- 15: the reaction product of the alkyl succinic anhydride of Example 2 with poly(ethylene glycol) having a number average molecular weight of about 880;
- 16: ethyl ester of alanine;
- 17: N-methyl stearamide;
- 18: butyloxazoline;
- 19: 2-ethylhexyl phosphate.

Examples 20-23

Example 2 is substantially repeated except that the substituted zinc salicylate from Example 1 is replaced by each of the following materials, in turn:

20: zinc salicylate.

21: an overbased zinc salicylate, wherein the salicylic acid is an alkyl salicylic acid, the alkyl group having a about 13 to about 18 carbon atoms, the salicylic acid having been treated (in an oil medium) with 3 equivalents of zinc hydroxide and carbon dioxide having been bubbled through the mixture to convert substantially all of the excess zinc hydroxide to the carbonate.

22: a zinc salt of alkyl salicylic acid (13-18 carbon atoms in the alkyl group), the zinc salt being a carbonate overbased salt having a metal ratio of about 6.

23: a zinc salt of alkyl salicylic acid (13-18 carbon atoms in the alkyl group), the zinc salt being a carbonate overbased salt having a metal ratio of about 20.

#### Examples 24-28.

Example 6 is substantially repeated except that the relative percentages by weight of the components are as indicated in the following Table:

Component\ Example:	24	25	26	27	28
Oil	96.1	99.9+	99.9	98.4	99.7
Thiophosphates	1.93	0.02	0.05	1.0	0.2
Zn salicylate	0.96	0.002	0.01	0.05	0.001
Succinic ester	1.0	0.01	0.04	0.5	0.1

#### Example 29.

A composition is prepared from 12 weight percent zinc O,O-di(isopropyl)dithiophosphate, 34 weight percent zinc O,O-di(2-ethylhexyl)dithiophosphate, 4 weight percent of a neutral zinc salt of alkyl salicylic acid, the alkyl group having about 13 to about 18 carbon atoms, and the balance mineral oil.

#### Example 30.

A composition is prepared from 23 weight percent zinc O,O-di(isopropyl)dithiophosphate, 66 weight percent zinc O,O-di(2-ethylhexyl)dithiophosphate, 8 weight percent of a neutral zinc salt of alkyl salicylic acid, the alkyl group having about 13 to about 18 carbon atoms, and the balance mineral oil.

#### Example 31.

A composition is prepared from 15 weight percent zinc O,O-di(isopropyl)dithiophosphate, 42 weight percent zinc O,O-di(2-ethylhexyl)dithiophosphate, 5 weight percent of a carbonate overbased zinc salt of alkyl salicylic acid, the alkyl group having about 13 to about 18 carbon atoms and the metal ratio being 6.2, and 23 weight percent of the reaction product of dodecyl substituted succinic anhydride, propylene oxide, and a small amount of water (to form a partial ester). The balance of the composition is 11% mineral oil and 4% dodecane.

#### Examples 32-34.

Each of the mixtures of Examples 29-31 is diluted with sufficient synthetic hydrocarbon oil to provide a composition having a concentration of zinc O,O-di(isopropyl)dithiophosphate of 0.4 weight percent.

#### Examples 35-36.

To 5 g of the composition of Examples 29 and 30, respectively, is added 3 g of polyethylene oxide of molecular weight 600 and 92 g water. Each mixture is stirred to form an emulsion.

Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials or reaction conditions are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material

which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. As used herein, the expression "consisting essentially of" permits the inclusion of substances which do not materially affect the basic and novel characteristics of the composition under consideration.

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## Claims

1. A functional fluid comprising a major amount of an oil of lubricating viscosity and
  - (A) about 0.05 to about 1 weight percent of at least one metal salt of
    - (i) a thiophosphoric acid or
    - (ii) a mixture of a thiophosphorus acid and a carboxylic acid;
  - (B) a zinc salt of a salicylic acid; and
  - (C) a rust inhibitor other than a compound of (A) or (B),
 provided that the functional fluid contains less than about 1% by weight of a dispersant and less than about 1% by weight of a basic sulfonate salt.
2. The fluid of claim 1 wherein (A) is present in an amount of from about 0.1% to about 2% by weight, (B) is present in an amount from about 0.001% to about 1% by weight, and (C) is present in an amount of about 0.01% to about 1% by weight.
3. A functional fluid comprising a major amount of an oil of lubricating viscosity and
  - (A) about 0.05 to about 1 weight percent of at least one metal salt of
    - (i) a thiophosphoric acid or
    - (ii) a mixture of a thiophosphorus acid and a carboxylic acid;
  - (B) about 0.001 to about 0.5 weight percent of a zinc salt of a salicylic acid;
 provided that the functional fluid contains less than about 1% by weight of a dispersant and less than about 1% by weight of a basic sulfonate salt.
4. The functional fluid of either of claims 1 and 2 wherein the rust inhibitor is a half ester of a hydrocarbyl-substituted succinic acid.
5. The fluid of any preceding claim wherein (A) is a zinc salt.
6. The fluid of any preceding claim wherein (A) is a basic metal salt.
7. The fluid of any preceding claim wherein the salicylic acid is a hydrocarbyl-substituted salicylic acid having from an average of about 7 to about 300 carbon atoms in the hydrocarbyl group.
8. The fluid of any preceding claim wherein (B) is an overbased salt.
9. A concentrate comprising about 3 to about 50 percent by weight of a carrier and about 50 to about 97 percent by weight of a mixture of:
  - (A) at least one metal salt of
    - (i) a thiophosphoric acid or
    - (ii) a mixture of a thiophosphorus acid and a carboxylic acid; and
  - (B) a zinc salt of a salicylic acid;
 provided that the concentrate contains less than about 5% by weight of a dispersant and less than about 5% by weight of a basic sulfonate salt.
10. The concentrate of claim 9 further comprising (C) a rust inhibitor other than a compound of (A) or (B).
11. An aqueous-based functional fluid comprising water, about 2 to about 10 weight percent of the composition of the concentrate of either of claims 9 and 10, and about 1 to about 5 weight percent of an emulsifier.
12. A method of improving thermal stability of a functional fluid, comprising the steps of preparing a mixture of a major amount of an oil of lubricating viscosity and
  - (A) at least one metal salt of
    - (i) a thiophosphoric acid or

(ii) a mixture of a thiophosphorus acid and a carboxylic acid, and  
(B) a zinc salt of a salicylic acid;  
provided that the function fluid contains less than about 1% by weight of a dispersant and less than about  
1% by weight of a basic sulfonate salt.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 93 31 0428

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	GB-A-1 137 819 (SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ) * page 1, line 32 - line 37 * * page 2, line 30 - line 34 * * page 2, line 36 - line 37 * * page 2, line 76 - line 78 *	1,2,5,7,8,12	C10M141/10 C10M159/20 C10M163/00 //C10N30/08, (C10M141/10, 129:26,129:54, 129:76, 137:10), (C10M159/20, 159:20), (C10M163/00, 129:26,129:54, 129:76,137:10, 159:20)
A	GB-A-2 083 073 (ESSO RESEARCH AND ENGINEERING COMPANY) ---	1,3,5,6,12	
D,A	US-A-4 466 894 (K.B. GROVER) * column 1, line 33 - line 36 * * column 1, line 65 - column 2, line 7 * * column 4, line 14 - line 16 * * claims 1,5 *	1,2,5,6,12	
A	US-A-2 907 714 (C.E. FRANCIS) * column 1, line 27 - line 30 * * column 2, line 11 - line 12 *	11	
D,A	US-A-2 261 047 (P.A. ASSEFF) -----		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.5)  C10M
Place of search THE HAGUE		Date of completion of the search 28 March 1994	Examiner Hilgenga, K
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document</p>			

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